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ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

Руководитель-эксперт Федерального государственного бюджетного учреждения науки Института элементоорганических соединений им. А.Н.Несмеянова Российской академии наук, рассмотрев *статью* Y. Zhang, A.V. Sokolov, A.V. Vologzhanina, T.V. Sudakova, J. Wang, E.V. Alexandrov «**Topologically guided exfoliation of 3D metal-organic frameworks into nanosheets**», подготовленную для печати в журнале *Mat.Chem.Phys.*, подтверждает, что в материале *не содержатся* сведения, предусмотренные Постановлением Правительства РФ №1233 от 30.11.1994г. и на публикацию материала *не следует* получать разрешение *Минобрнауки и/или Президиума РАН*

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Topologically guided exfoliation of 3D metal-organic frameworks into nanosheets

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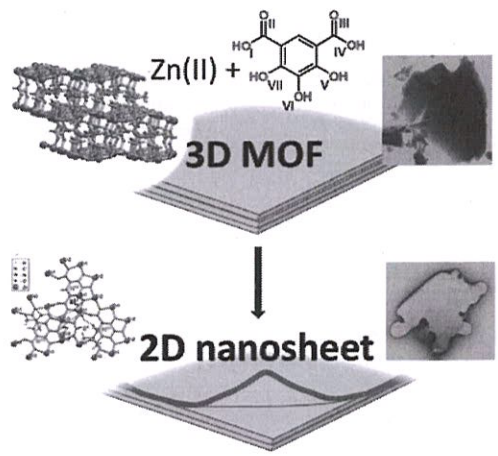
HIGHLIGHTS

- Topological tools are applied for predicting 3D MOFs to 2D nanosheets exfoliation.
- A new compound $[Zn_4(THIP)(HCO_2)_3(H_2O)_4]\bullet DMF$ was synthesized using 4,5,6-trihydroxyisophtalic acid (H_5THIP) and exfoliated.
- The nanosheets of height 0.1–90 nm and lateral sizes above 400 nm are good candidates for coating and nanoparticles support.

GRAPHICAL ABSTRACT



ABSTRACT

Herein a general concept for screening 3D metal-organic frameworks (MOFs) for 2D nanosheets design is presented. Active coordination centers and terminal ligands of 3D-to-2D MOF nanosheets can result in self-assembly of multilayer structures. In comparison to 2D MOFs, 3D frameworks can provide nanosheets with better adhesion, strength, adsorptive capacity and catalytic activity. They are also promising in semiconductors, sensorics, and drug delivery systems. However, less than a dozen of 3D-to-2D MOF nanosheets have been produced to date. Therefore, we applied topological tools of ToposPro and Cambridge Structural Database for screening 3D MOFs as sources of new 2D nanosheets. Cluster representation uncovered the potential existence of 2D nanosheets as subnets of 3D networks in 3032 structures. Furthermore, parameters of building units, net topologies, and accessible channels were analyzed. The concept was proved by synthesis and successful exfoliation of new compound $[Zn_4(THIP)(HCO_2)_3(H_2O)_4]\bullet DMF$ (**1**), which was assembled from 4,5,6-trihydroxyisophtalic acid (H_5THIP) as intralayer linker, formate

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4. Conclusions

Computer tools for topological analysis open up plenty of new research directions in nanomaterials design. ToposPro program package was applied for analysis of 3056 topological representations of 3D MOFs (from CSD) with 2D SBUs interconnected by coordination bonds. It was shown that these structures have potential as sources of new nanosheets. Cluster topological representations provided topological prerequisites for predicting exfoliation and possible nanosheets morphology. The high ratio of average coordination number of nanosheet to average number of interlayer pillars incident to nodes, presence of only chelating modes of ligands inside of nanosheets, larger length of the shortest interlayer edge, and wide accessible channels were suggested as factors promoting exfoliation. Possible routs for designing nanosheets were organized into the form of decisions tree. New compound $[Zn_4(THIP)(HCO_2)_3(H_2O)_4]\bullet$ DMF was synthesized and assigned to the most frequent pattern in the decisions tree. The nanosheets of the compound with height 0.1–90 nm were produced by exfoliation technique that further proves the general concept. We encourage the scientific community to continue studies of exfoliation for other categories of 3D MOFs in the decisions tree and searches of practical applications for them. Further accumulation of the experimental data will allow development of machine learning techniques for predicting exfoliation.

CRediT authorship contribution statement

Yaxin Zhang: Writing – original draft, Visualization, Formal analysis, Data curation. **Andrey V. Sokolov:** Writing – original draft, Resources, Methodology. **Anna V. Vologzhanina:** Writing – original draft, Resources, Methodology. **Tatyana V. Sudakova:** Methodology. **Junjie Wang:** Writing – review & editing. **Eugeny V. Alexandrov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Eugeny Alexandrov reports financial support was provided by Russian Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchemphys.2024.129804.

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